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## Fourier Transform Infrared Study on the Phase Transitions of a Sodium Dodecyl Sulfate-Water System

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Fourier transform infrared spectroscopy has been used to study thermotropic phase transitions of a sodium dodecyl sulfate (40 g%)-water system. The main transition in this system is that from liquid crystal to Coagel I, being observed at 23.5°C. It is found that the ice forming of free water at 0°C induces a new metastable coagel phase (Coagel II). Besides, annealing at -20°C results in a formation of another stable coagel phase (Coagel III). Spectroscopic and structural features of the hydrophilic and hydrophobic groups of the surfactant are discussed in each phase, together with those of water.

KEY WORDS: SDS/ Sodium dodecyl sulfate/ FT-IR/ Fourier transform infrared spectra/ Coagel/ Liquid crystal/ Phase transition/

### INTRODUCTION

Sodium n-dodecyl sulfate (SDS) is a most typical anionic surfactant, and physical properties of its aqueous solutions have been studied by many workers, especially at low surfactant concentrations. However, only a limited number of papers have dealt with the properties at high SDS concentrations or at low temperatures. As to the lyotropic mesomorphic phases, the X-ray studies by Luzzati *et al.*,<sup>1-3)</sup> the differential thermal analysis by McDonald *et al.*,<sup>4)</sup> the density and electric conductivity measurement by Yano *et al.*,<sup>5)</sup> and the Fourier transform infrared (FT-IR) study by Mantsch *et al.*<sup>6)</sup> may be cited. In these papers, none has covered the temperature range below 0°C.

Herein we have recorded FT-IR spectra of a 40 g% SDS-water system in a temperature range -20°C to +44°C. In this system, the phase transition from coagel to liquid crystal (middle or hexagonal phase) was found to occur at 23.5°C, being in good agreement with the phase diagram drawn by Fontell.<sup>7)</sup> Attention was focused on the effect of water freezing and of annealing upon the coagel structure.

### EXPERIMENTAL

#### Material and sample cell

High purity (>99%) SDS was purchased from Nakarai Chemicals, Ltd., Kyoto. A mixture of 40 g% (1.5 M) SDS and 60 g% doubly distilled water in a vial was allowed to stand for 5 hours at 50°C before measurements. A demountable liquid cell (model DLC-M25) from Harrick Scientific Corp., Ossining, N.Y. was employed with wedged calcium fluoride windows. The assembly of the cell was achieved as

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quick as possible to prevent the water loss by evaporation. No spacer was used and hence the sample thickness is estimated to be a few  $\mu\text{m}$ . The temperature is monitored by a copper-constantan thermocouple inserted between a window edge and an O-ring. The sample cell was placed in a mount thermostated by a Neslab model RTE-8 refrigerated bath circulator with a 1 : 1 mixture of ethyleneglycol and water. The overall accuracy of temperature control and reading was within  $\pm 0.1^\circ\text{C}$ , as deduced from measurements of ice-melting and so forth.

### Thermal hystereses of samples and FT-IR measurements

The gel phase (transparent and microscopically homogenous system) or coagel phase (opaque and microscopically inhomogenous system with hydrated crystals and water) of amphiphilic substances often takes supercooled metastable states. Thus, the actual state of a sample depends on its thermal hysteresis.<sup>8-10)</sup> In the present work, two kinds of samples with different thermal hystereses were prepared.

Sample A was once cooled down to  $-14^\circ\text{C}$  from room temperature and was then subjected to FT-IR measurements during heating process. On the other hand, Sample B was annealed at  $-20^\circ\text{C}$  for 12 hours and then heated up. In both samples, the rate of heating of the bath circulator was  $\sim 0.5^\circ\text{C}/\text{min}$ . After the temperature of the bath circulator reached each set point, 15 minutes were wasted to assure the temperature equilibrium of the sample. Then, a FT-IR spectrum was measured with 1000 scans in another 15 minutes. Both samples exhibited the phase transition from coagel to liquid crystal at  $23.5^\circ\text{C}$ .

Spectra were recorded on a Nicolet model 6000 Fourier transform infrared spectrophotometer with an MCT detector. The maximum optical retardation of 0.25 cm, Fourier transformation with one-level of zero filling, and Happ-Genzel apodization function were used to yield a resolution better than  $4\text{ cm}^{-1}$ .

## RESULTS

### Spectra of unannealed Sample A

Infrared spectra of unannealed Sample A in the  $3850\text{--}2800$  and  $1700\text{--}1000\text{ cm}^{-1}$  regions are shown in Figs. 1 and 2, respectively. When we successively look at the spectra from top to bottom in these figures, we notice several points. First, spectral changes expected upon the phase transition from liquid crystal to coagel are easily recognized in the  $1100\text{--}1000\text{ cm}^{-1}$  region of the spectra between  $25.0$  and  $22.5^\circ\text{C}$ . Second, if we compare the coagel spectra below and above  $0^\circ\text{C}$ , apparent differences are found not only for water bands around  $3300$  and  $1620\text{ cm}^{-1}$  but also for many SDS bands in the  $1500\text{--}1000\text{ cm}^{-1}$  region, the spectrum at  $2^\circ\text{C}$  being somewhere in the middle of the two. This finding which indicates the presence of another phase transition around  $0^\circ\text{C}$  does not seem general in amphiphilic substance-water systems.<sup>11)</sup> Herein we call the coagel phases above and below  $0^\circ\text{C}$  as Coagel I and Coagel II phases, respectively.

### Spectra of annealed Sample B

Infrared spectra of annealed Sample B in the  $3850\text{--}2800$  and  $1700\text{--}1000\text{ cm}^{-1}$  regions are given in Figs. 3 and 4, respectively. The spectra of Sample B above

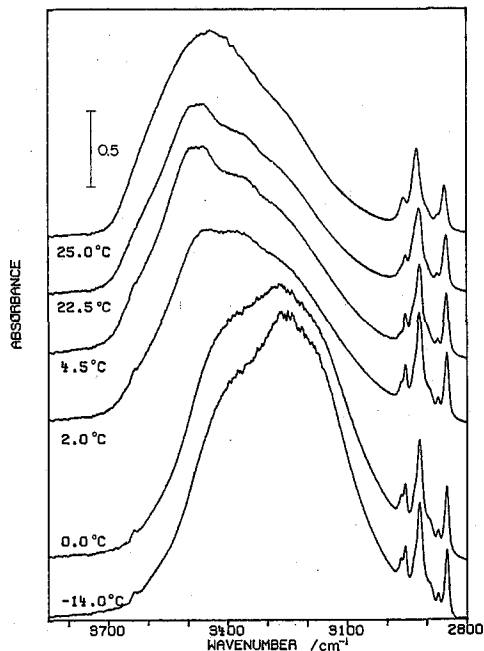


Fig. 1. Infrared spectra of Sample A (40 g% SDS-water, unannealed) in the 3850-2800  $\text{cm}^{-1}$  region at several temperatures.

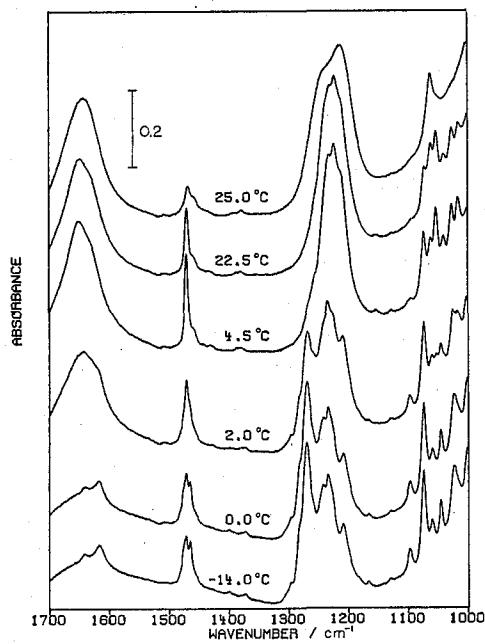


Fig. 2. Infrared spectra of Sample A (40 g% SDS-water, unannealed) in the 1700-1000  $\text{cm}^{-1}$  region at several temperatures.

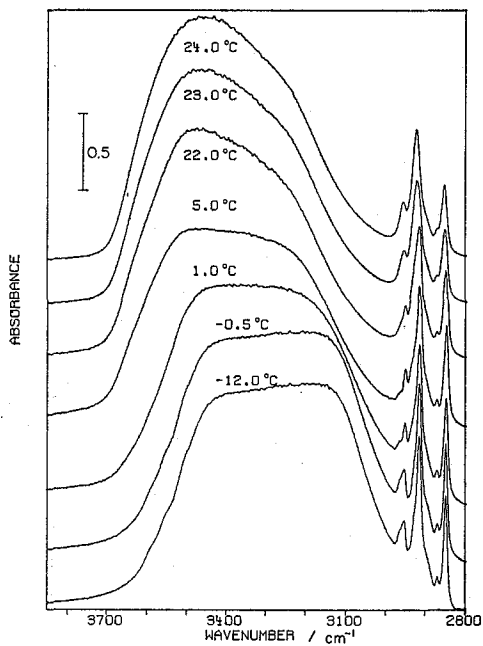


Fig. 3. Infrared spectra of Sample B (40 g% SDS-water, annealed) in the 3850-2800  $\text{cm}^{-1}$  region at several temperatures.

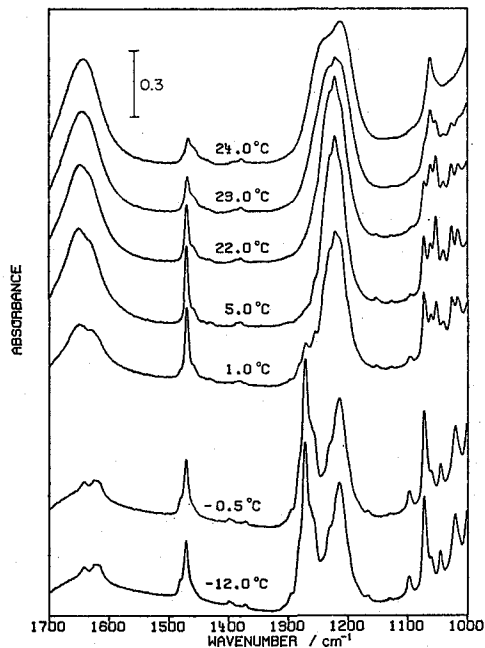


Fig. 4. Infrared spectra of Sample B (40 g% SDS-water, annealed) in the 1700-1000  $\text{cm}^{-1}$  region at several temperatures.

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0°C almost coincide with those of Sample A in Figs. 1 and 2. However, appreciable differences can be found between the spectra of Samples A and B below 0°C, especially in the 1500–1200 cm<sup>-1</sup> regions. We repeated cooling and heating cycles between -20 (or -14) and +45°C several times with (or without) annealing for a single sample,

 Table I. Observed infrared bands of SDS and water in the various phases.<sup>a</sup>

Liquid crystal +24°C <sup>b</sup>	Coagel I +5°C <sup>b</sup>	Coagel II -10°C	Coagel III -10°C	Assignment <sup>c</sup>
~3450 s	[~3475 s ~3350 sh]	~3400 sh	~3400 sh	ν(OH) <sup>d</sup>
~3250 sh	~3250 sh	~3250 s	~3180 s	
2957.7 m	[2968.7 sh 2953.2 m]	2968.1 w	2968.2 sh	ν <sub>a</sub> (CH <sub>3</sub> )
2924.5 s	2916.5 s	2918.1 s	2917.0 s	
2872.3 sh	2873.0 m	2871.7 m	2871.6 m	ν <sub>s</sub> (CH <sub>3</sub> )
2854.4 s	2849.2 s	2849.1 s	2850.3 s	ν <sub>a</sub> (CH <sub>2</sub> )
1643 s	[1650 s ~1633 sh]	1641 w	1642 w	δ(HOH) <sup>d</sup>
~1477 sh	—	1617 m	1623 m	
1467.6 m	1470.5 s	[1471.8 m 1465.4 m]	1471.5 m	δ(CH <sub>2</sub> )
~1459 sh	~1460 sh	~1455 sh	~1459 sh	ν <sub>a</sub> (SO <sub>3</sub> <sup>-</sup> )
1390 sh	~1388 w	1400.1 w	1399.0 w	
1378.5 w	1380.0 w	1372.4 w	1371.6 w	
—	—	~1295 sh	~1294 sh	
—	~1274 sh	~1281 sh	~1283 sh	ν <sub>a</sub> (SO <sub>3</sub> <sup>-</sup> )
~1244 sh	—	1269.4 s	1272.3 s	
—	~1235 sh	1241.6 sh	~1256 sh	
—	1222.6 s	1233.7 s	~1232 sh	
1213.0 s	~1210 sh	1208.4 m	1214.6 s	ν <sub>s</sub> (SO <sub>3</sub> <sup>-</sup> )
—	1153.1 w	1166.1 w	1167.2 w	
—	1127.8 w	1129.5 w	1130.1 w	
—	1093.7 w	1097.2 m	1097.1 m	
1062.2 m	1072.6 m	1074.2 s	1072.6 s	ν <sub>s</sub> (SO <sub>3</sub> <sup>-</sup> )
—	1061.5 w	1059.5 m	1061.1 sh	
—	[1052.7 m 1040.0 m]	1045.3 m	1045.5 m	
—	[1026.1 m 1015.6 m]	1023.1 m	1020.3 m	

<sup>a</sup> s, strong; m, medium; w, weak; sh, shoulder.

<sup>b</sup> The wavenumber is the average between Samples I and II.

<sup>c</sup> ν, stretching; δ, bending; a, asymmetric or antisymmetric; s, symmetric.

<sup>d</sup> water bands.

<sup>e</sup> Ref. 6.

and confirmed the reproducibility of the change due to annealing. Thus, the Coagel II phase of unannealed Sample A can be regarded as a metastable phase, the coagel phase of annealed Sample B below 0°C (we call it Coagel III phase, here) being a stable phase. The observed infrared bands of SDS in each phase are summarized in Table I, with assignment when possible.

## DISCUSSION

### Coagel II-Coagel I phase transition

#### *Water bands*

In the SDS concentration of 40 g%, the molar ratio of SDS and water is 1 : 24. Since the saturated amount of bound water in SDS-water systems is reported to be 10–13 molecules per one SDS molecule,<sup>12)</sup> Sample A is expected to contain the comparable amount of bound water and free water. In fact, the spectra of Coagel II below 0°C (Figs. 1 and 2) exhibit the ice peaks<sup>13)</sup> at about 3250 and 1641 cm<sup>-1</sup> originated from free water in Coagel I above 0°C. The band around 1620 cm<sup>-1</sup> in Coagel II below 0°C appears as a shoulder band in Coagel I and can be ascribed to the bound water.<sup>14)</sup> The O–H stretching band of water in Coagel I at 4.5 or 22.5°C (Fig. 1) exhibits a complex band contour with bumps at about 3475 and 3350 cm<sup>-1</sup>, as compared with the simple contour at 25°C which is very similar to that of liquid water.<sup>13)</sup> This complex contour in the Coagel I may be also ascribed to the bound water in the coagel phase.

#### *The asymmetric SO<sub>3</sub><sup>-</sup> stretching band*

The distinction of Coagels I and II arises from the state of free water. Thus, structures of hydrophilic groups would be largely affected by the phase transition. The asymmetric SO<sub>3</sub><sup>-</sup> stretching band, expected in the region 1300–1200 cm<sup>-1</sup>,<sup>6)</sup> of the Coagel II phase below 0°C (Fig. 2) consists of at least four peaks. As the asymmetric SO<sub>3</sub><sup>-</sup> stretching mode is normally degenerated, the band may become a doublet as a result of symmetry lowering in the crystalline coagel. Further, the two components of the doublet can be split into four due to the effect of crystal field. In the Coagel I phase at 4.5 and 22.5°C, the band gets more simple in feature. This indicates that the states of the hydrophilic SO<sub>3</sub><sup>-</sup> group are strongly affected by the ice melting due to free water.

#### *The CH<sub>2</sub> scissoring band*

The CH<sub>2</sub> scissoring band of alkyl chain is often utilized to get informations about molecular packings of the chain in solid-like phases.<sup>15,16)</sup> As is found in Fig. 2 and Table I, the band in the Coagel II phase below 0°C appears as doublet, while it is singlet in Coagel I. The observed wavenumber is plotted against temperature in Fig. 5. The doublet below 0°C univocally identifies itself with an orthorhombic sub-cell packing of the alkyl chain illustrated in the left-hand side of Fig. 6.<sup>15,16)</sup> The peak wavenumber, ~1470 cm<sup>-1</sup>, of the single band in the Coagel I phase is too high to be ascribed to a hexagonal subcell packing (the right-hand side of Fig. 6) whose wavenumber is expected just around that of the liquid crystal phase (1467.5 cm<sup>-1</sup> as shown in Fig. 5).<sup>11)</sup> In connection with this, Mantsch *et al.*<sup>9)</sup> have observed the

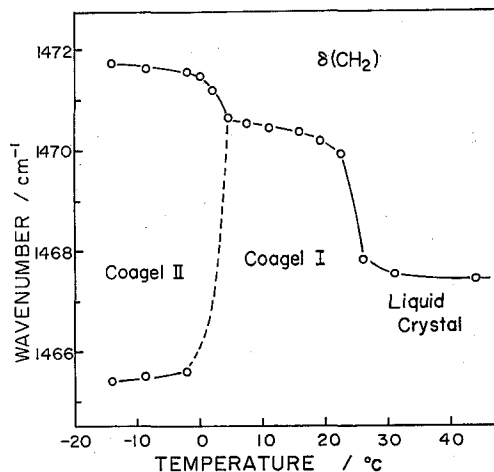


Fig. 5. Temperature dependence of the wavenumber of the  $\text{CH}_2$  scissoring band of Sample A (40 g% SDS-water, unannealed).

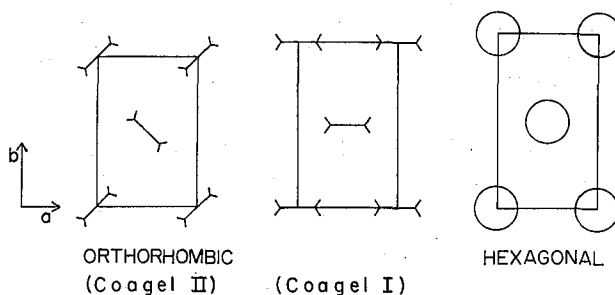


Fig. 6. The idealized subcell of the hydrocarbon chains in the Coagel I phase (center) compared with orthorhombic and hexagonal subcells.

$\text{CH}_2$  scissoring band of sodium hexadecylsulfate in a coagel phase at  $1473\text{ cm}^{-1}$  and tentatively ascribed it to alkyl chains packed in a triclinic subcell. On the other hand, Sundell<sup>17)</sup> has performed an X-ray analysis of a  $\text{SDS} : \text{H}_2\text{O}$  ( $=8 : 1$ ) complex and concluded that the chain packing can be described as an intermediate between the orthorhombic and hexagonal chain packing modes, with the two-fold symmetry along the chain axis (as illustrated in the center of Fig. 6). This packing resembles the orthorhombic parallel packing found in the crystal of hexadecyltrimethylammonium dichloriodide.<sup>18)</sup> Therefore, it is most likely that a chain packing similar to the structure shown in the center of Fig. 6 also occurs in the Coagel I phase of the present SDS-water system. The gradual wavenumber decrease with temperature in the Coagel I phase in Fig. 5 may imply the increased irregularity of the chain packing with temperature.

#### *CH stretching bands*

The temperature dependences of the wavenumber of the asymmetric  $\text{CH}_3$  and antisymmetric  $\text{CH}_2$  stretching bands of unannealed Sample A are given in Fig. 7.

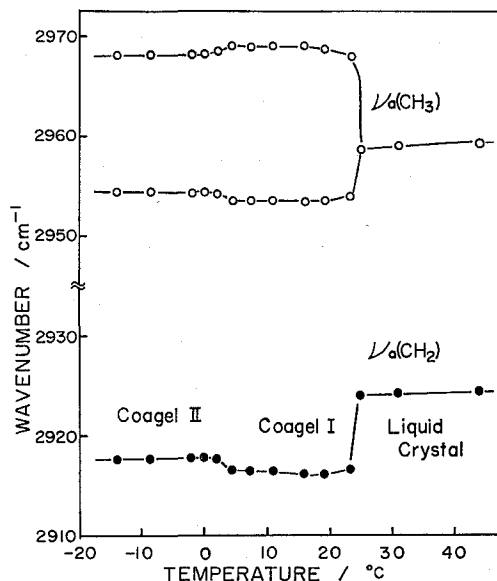


Fig. 7. Temperature dependence of the wavenumber of the asymmetric  $\text{CH}_3$  and antisymmetric  $\text{CH}_2$  stretching band of Sample A (40 g% SDS-water, unannealed).

These bands are sensitive to the change in molecular environment surrounding the alkyl chain and particularly the latter band to the change in molecular conformations.<sup>20)</sup> The wavenumber shift upon the phase transition from Coagel II to Coagel I is minimal in these bands, indicating that the ice melting and the concomitant change in chain packing do not much affect the conformation and molecular environment of the alkyl chain.

The asymmetric  $\text{CH}_3$  stretching band is split into two components in the Coagel I and II phases in Fig. 7. This implies that the internal rotation of the terminal  $\text{CH}_3$  group is highly restricted in these phases.<sup>19)</sup>

#### Coagel I-liquid crystal phase transition

The bumps at 3475, 3350, and 1620  $\text{cm}^{-1}$  (Figs. 1 and 2) assignable to the vibrations of bound water in the Coagel I phase disappears in the spectra of liquid crystal at 25°C. The OH stretching and HOH bending bands of water in the liquid crystal phase are practically the same as those of liquid water.<sup>13)</sup> This may imply that the structure of bound water textured in the stable network of ionic layers of Coagel I phase collapses under the increased mobility of ions and SDS molecules in the liquid crystal phase. The increased mobility of the SDS molecule makes all the SDS bands broad.

The  $\text{CH}_2$  scissoring band appears at 1467.5  $\text{cm}^{-1}$  in the liquid crystal phase (Fig. 5). This wavenumber is typical of the alkyl chain in the disordered liquid-like state.<sup>16)</sup> The disordered state of the alkyl chain can be also inferred from the wavenumber of the antisymmetric  $\text{CH}_2$  stretching band above 24°C in Fig. 7 and Table I.<sup>21)</sup> The disappearance of many bands in the C-C stretching region (1100–1000



$\text{cm}^{-1}$ ) of Coagel I (Fig. 2) is also related to the collapse of trans zigzag structure of the alkyl chain.<sup>22)</sup>

As is clear from Fig. 7, the asymmetric  $\text{CH}_3$  stretching band becomes singlet in the liquid crystal phase, indicating the presence of free rotation of the methyl group in that phase.<sup>20)</sup>

### Coagel III phase

The Coagel III phase, which appears upon annealing at  $-20^\circ\text{C}$ , exhibits some characteristic features in the spectra of hydrophilic part. The asymmetric  $\text{SO}_3^-$  stretching band of the Coagel III phase below  $0^\circ\text{C}$  is split into two strong components at  $1272$  and  $1215\text{ cm}^{-1}$ , with shoulders at  $1256$  and  $1232\text{ cm}^{-1}$  (Fig. 4). This offers a marked contrast with the band in the Coagel II phase (Fig. 2). The spectral feature of the band in the Coagel III phase rather resembles to that of the coagel of sodium hexadecylsulfate just below the critical micellization temperature.<sup>6)</sup> The wavenumbers and band shapes of this band is reported to be strongly dependent on the electrostatic interactions and counter-ion binding.<sup>6)</sup> Thus, the stable Coagel III phase may be brought about by molecular rearrangements in the hydrophilic ionic layers including bound water during annealing. In fact, the OH stretching band of water in Coagel III below  $0^\circ\text{C}$  (Fig. 3) gives more smooth feature than the Coagel II (Fig. 1).

Another characteristic point of the Coagel III phase is the packing of the alkyl chain. The temperature dependence of the wavenumber of the  $\text{CH}_2$  scissoring band of Sample B is presented in Fig. 8. The band appears as singlet at  $1471.5\text{ cm}^{-1}$ ,  $1\text{--}1.5\text{ cm}^{-1}$  higher than the Coagel I phase. Thus, the packing in the Coagel III phase may be very close to that in Coagel I (the packing shown in the center of Fig. 6). A triclinic subcell is also admissible from this fact only.<sup>6)</sup> However, if the four bands in the  $1300\text{--}1200\text{ cm}^{-1}$  of the Coagel III phase (Fig. 4 and Table I) are due to the asymmetric  $\text{SO}_3^-$  stretching mode as in the case of the Coagel II phase mentioned above, the space group cannot be triclinic, indicating that the subcell is not triclinic.

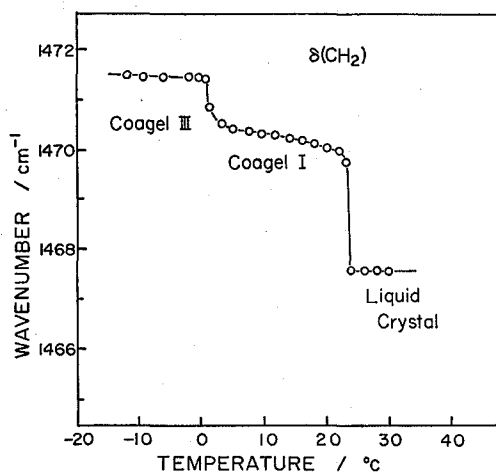


Fig. 8. Temperature dependence of the wavenumber of the  $\text{CH}_2$  scissoring band of Sample B (40 g% SDS-water, annealed).

Since we have not measured polarized spectra of oriented samples, we cannot conclude whether the subcell is triclinic or not for the present. In either case, however, the singularity and the peak position of the  $\text{CH}_2$  scissoring band indicate the parallel packing of the trans zigzag plane of the alkyl chain.

It is also noted in Fig. 8 that the phase transition from Coagel III to Coagel I occurs in a narrower temperature region than that from Coagel II to Coagel I (Fig. 5). In the latter case, the transition occurs gradually after the ice-melting at  $0^\circ\text{C}$ , ending at about  $4.5^\circ\text{C}$ . In the former case, however, the transition almost finishes at  $1^\circ\text{C}$ . The temperature width of transition seems to be related with the metastability (or stability) of the coagel phase.

### Concluding remarks

The present work demonstrates that the ice-melting affects the molecular structure and packing of the SDS coagel phase, inducing a phase transition. The effect of annealing at low temperature was also presented. Since this experiment was performed only at one SDS concentration, the full understanding of the structural aspect of phases in SDS-water system still awaits further clarifications. However, it became clear that the FT-IR method provided a rather easy and reliable way of studying phase changes in amphiphile-water systems.

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